COAL SOLUBILIZATION BY NON-CATALYTIC TRANSFER HYDROGENATION WITH FORMATE

Soon Chuan Lim and Edwin N. Givens
University of Kentucky, Center for Applied Energy Research
3572 Iron Works Pike, Lexington, KY 40511-8433

Abstract

Non-Catalytic transfer hydrogenation using formate as the hydrogenating agent significantly reduces the severity necessary for solubilizing coal. Moisture and mineral matter free solubilization of coal up to 94% in pyridine was observed for a Wyodak coal that was treated at 340 °C for 1 hr with CO and aqueous NaOH. Loss of oxygen from coal as CO_2 agrees with a forced balance based upon elemental and mass recoveries. A hydrogen consumption of 0.6 wt %, calculated from this balance, agrees with hydrogen consumptions independently determined based upon CO conversion. The hydrogen to carbon ratio in the total water-insoluble product increased to 0.88 versus a corresponding value of 0.80 in the starting coal. The pyridine soluble and insoluble fractions had H/C values of 0.97 and 0.59, respectively. Reaction in the absence of added salt produced a water-insoluble product that was 50% soluble in pyridine and had a H/C value of 0.79.

Introduction

CO-promoted hydrothermal treatment of low-rank coals has been found by several groups to be quite effective for converting these coals to soluble products.[1] A group at Exxon reported that hydrothermal treatment of a Wyoming subbituminous coal in the presence of CO at 345 °C for 6 hours produced a material that was largely soluble in THF and was more soluble than material produced by hydrothermal treatment in the absence of CO.[2] Treating the coal under the same conditions in decalin failed to increase the solubility relative to that of the raw coal. Hydrothermal treatment substantially depolymerized the coal making it more reactive for producing distillate product in a hydrogen donor solvent.[2,3] The hydrothermal product was enriched in hydrogen and had reduced oxygen content. The CO-aqueous system presumably promotes decarboxylation of oxygen-containing constituents and cleavage of ether and ester groups attached to aromatic ring systems. Under these reaction conditions, a Martin Lake, Texas lignite heated in $^{13}CO/D_2O$ was shown to produce formate ion with most of the deuterium in the reacted D_2O being transferred into the coal.[4] The recovered CO_2 contained 60% $^{12}CO_2$ from the coal, presumably formed via decarboxylation, and 40% $^{13}CO_2$ from ^{13}CO via the water-gas-shift reaction. Adding alkali metal salts to the CO/H_2O mixture presumably increases the concentration of formate ion further enhancing the solubility of the product.[5] In the work reported here, the reactivity of a Wyodak coal under hydrothermal conditions in the presence of CO and sodium hydroxide is discussed.

Experimental

Wyodak coal from the Black Thunder mine in Wright, Wyoming, was ground to -200 mesh, riffled and stored in tightly sealed containers. Ultimate analysis: carbon, 73.9%; hydrogen, 5.2%; nitrogen, 1.3%; sulfur, 0.6%; oxygen, 19.0% (by difference). Ash content (dry basis) was 6.12 wt%. All results are expressed as weight percent moisture and ash-free coal (maf).

In the experiments conducted in a 300 ml stirred autoclave, 50 g of as-received coal containing approximately 20% moisture were mixed with 4.2 g NaOH in 75 ml. of distilled and de-ionized water. The reactor was sealed, leak tested and pressurized with CO to 1000 psig. In experiments in the absence of base, only 40 ml of water was added. Heat-up time from ambient to reaction time at 340 °C was approximately 3.5 hr. The reaction was allowed to proceed at this temperature for an additional hour. The reactor was cooled to ambient temperature within 1.5 hr. A gas sample was collected and analyzed by gas chromatography and the solid products were removed from the reactor, washed with distilled and de-ionized water and dried at 40 °C under vacuum. Soluble humic acids were recovered from the aqueous phase by precipitating the colloidal material with HCl (pH 1-2) followed by centrifugation and drying. The acidified aqueous layer was further extracted with ether. Product distribution and recovery of water-insoluble product, humic acids and ether solubles, on a maf basis, are shown in Table 1. A 5 g sample of the water-insoluble product was extracted with THF in a Soxhlet thimble for 18 hours. The Soxhlet extraction technique was exceptionally slow since colored material continued to exude from the thimble after a week of continuous extraction. A smaller sample (0.5 g) of product was placed in 200 mL of pyridine or THF and extracted using a sonication/vacuum filtration

technique at ambient temperature. Samples ultrasonicated in either solvent for 10 min filtered rapidly within minutes under vacuum at ambient temperature. Material was collected after solvents were removed, dried overnight at 80 °C at 16 kPa and weighed to determine solubility in the solvent. A reliable pyridine solubility value could not be obtained for the water-insoluble product from treating coal in the absence of NaOH. Material that was ultrasonicated in pyridine clogged the filter paper within minutes. The same material also clogged the Soxhlet thimble filters which resulted in less material dissolving in pyridine than in THF (see Table 2). This underscores the different properties of the material generated when salt was present during the reaction.

Discussion

The water-gas-shift reaction in the presence of NaOH is quite sensitive to temperatures between 250 and 340 °C with CO conversion increasing from <10% up to approximately 90%, respectively. At 300 °C in the presence of ~0.3 M NaOH, the conditions under which many of the earlier runs were made, the shift reaction goes to the extent of about 20-25%. In the absence of NaOH, the CO conversion at 340 °C is only ~40%. At 300 °C, very little H_2 is actually recovered, most of it being incorporated into the water-insoluble product. At 340 °C, about half of the H_2 that is formed is recovered. In every case, the amount of hydrocarbon gases formed in the reaction was quite small.

The amount of humic acids and ether-extracted material (fulvic acids) in the aqueous phase was small, being 1.3% in the presence of NaOH. The highest yields of these products (~7%) were observed at 300 °C, either at low CO pressures or in the absence of CO. Solubility of the water-insoluble material indicates the degree to which reaction occurred. Previously, solubilities in THF and pyridine were determined using a Soxhlet apparatus. The materials generated at 340 °C could not be evaluated in this manner since the extraction thimbles readily blinded. It was found that solubilities of the NaOH treated materials in these two solvents could be determined at ambient temperature using a sonication technique in which the extracted THF and pyridine solutions filtered quite readily without blinding the filter paper. Higher pyridine and THF solubilities were obtained using the ultrasonication technique compared to Soxhlet extraction. For the reactions run with NaOH, pyridine and THF solubilities reached 94 and 78 wt % (maf product basis), respectively. The ultrasonication technique could not be used on the product produced in the absence of added NaOH since it readily blinded the filter paper when filtered.

Chemical compositions of water-insoluble product and the solvent-separated fractions from the NaOH treated coal are shown in Table 3. For the 82.3 wt % of water-insoluble product plus humic acids, the 8% ash content was too high relative to the 5.5% concentration in the starting coal. In the absence of NaOH the ash content was closer to the expected value. In both cases, there was a decrease in the oxygen content from 17.9% in the starting coal to 4.7% in the water-insoluble product for the NaOH-treated coal and 5.2% for the NaOH-free case. Approximately 75% of the oxygen was removed in both cases. The hydrogen-carbon ratio for the NaOH-treated coal increased to 0.88 versus a value of 0.80 for the starting coal. By contrast, the H/C ratio of the product generated in the absence of base is essentially the same as that of the starting coal, indicating a loss of hydrogen in the reaction. The hydrogen concentration in the pyridine soluble fraction (0.97 H/C) is higher than in the starting coal (0.80 H/C), whereas the concentration in the insoluble fraction is much less (0.59 H/C). Oxygen concentration is much higher in the insoluble fraction. Note that the oxygen values for the solvent separated fractions are higher than observed in the water-insoluble product. This suggests a possible reactivity upon exposure to air since no special precautions were followed in handling these samples. The concentrations of nitrogen and sulfur in the solvent separated products are similar to the total water-insoluble product suggesting enrichment of nitrogen in the pyridine insoluble product.

Mass and elemental balances were calculated for the 300 mL autoclave experiments. The balance for the experiment run in the presence of NaOH, as shown in Table 4, was calculated by correcting the ash concentration in the water-insoluble product, which includes the humic acids and ether-soluble product, to a level consistent with the ash in the starting coal and adjusting the remaining elements to account for this correction. Since the gas analysis showed that hydrocarbon gases were quite small (see Table 1) the other products are water, CO and CO_2. Because very large concentrations of CO are present as a reactant and much of the CO_2 is formed as a result of the water-gas-shift reaction, the amount of these carbon oxides that are formed from carbon in the coal cannot be measured directly. The ratio of the additional oxygen and carbon needed to force the balance of these two elements in the product is greater than the 2 to 1 ratio in CO_2. Therefore, in the product, of the 78% of the oxygen in the starting coal that was absent from the water-insoluble product, most was present as CO_2 (60% of the original oxygen) with the remaining 18% of the original oxygen being present as

water. Formation of CO_2 is consistent with the results of Horvath and Siskin.[4] The hydrogen necessary to form the water was 0.42 wt % of ash-free coal, while the total hydrogen consumed in the reaction was ~0.6 wt % of the coal. Using these assumptions, all of the starting material is accounted for in the products.

The elemental balance for the experiment made in the absence of NaOH (see Table 5) showed that more carbon and less hydrogen was recovered in the water-insoluble product than for the NaOH treated coal. In fact, the amount of hydrogen was less than in the starting coal. Forcing a carbon balance indicated that less oxygen could be removed as CO_2 and the amount of water necessary to balance the oxygen was much higher. Of the 75% of oxygen removed from the coal, 23% was removed as CO_2 and 52% as water. The net H_2 consumption of 1.0 wt % hydrogen, which would have been formed via the water-gas-shift reaction, accounted for 85% of the hydrogen incorporated into the water. The remaining hydrogen came from the coal accounting for the decrease in hydrogen in the water-insoluble product.

The heating value of the treated coals were calculated using the equation developed by Boie and used by Ringen and co-workers.[6]

$$H_g(cal/g) = 8400C + 27765H + 1500N - 2500S - 26500$$

where H_g is the gross heating value and C, H, N, S and O are the normalized weight fractions of these elements in the sample. Multiplication by the factor 1.8 converts the results to units of Btu/lb.

	with NaOH	without NaOH	Coal
Heating Value, Btu/lb maf	16,400	16,000	12,900

The heating values for both CO-treated coals were significantly higher than the starting coal.

Summary

Reacting Wyodak coal with CO and H_2O at 340 °C, both in the presence and absence of base, produced materials having reduced oxygen contents. Oxygen removals in excess of 75% were obtained regardless of whether base was present. Addition of base gave a material which was highly soluble in both pyridine (95%) and THF (78%), whereas the solubility of the material produced in the absence of base was less. Water-insoluble materials produced in both cases had significantly higher heating values than the starting coal. Forced elemental balances based upon the absence of any significant hydrocarbons in the gaseous product provides insight into the probable reaction pathways for removal of oxygen. In the presence of base, a large part of the oxygen leaves as CO_2 while in the absence of base the water pathway is far more dominant. In both cases, the significant removal of oxygen can have a large economic impact on processing costs for low rank coals.

References

1. Lim, S. C.; Rathbone, R. F.; Rubel, A. M.; Givens, E. N.; Derbyshire. F. J. Energy and Fuels, 1994, 8, 294
2. Stuntz, G. F.; Culross, C. C.; Reynolds, S. D. United States Patent No. 5,026,475, June 25, 1991.
3. Vaughn, S. N.; Siskin, M.; Katritzky, A.; Brons, G.; Reynolds, N.; Culross, C. C.; Neskora, D. R. United States Patent No. 5,151,173; Sept. 29, 1992.
4. Horvath, I. T.; Siskin, M. Energy Fuels 1991, 5, 933-934.
5. Ng, F. T. T.; Tsakiri, S. K. Fuel 1993, 72, 211.
6. S. Ringen, J. Lanum and F.P. Miknis Fuel, 1979, 58, 69

Table 1. Product distribution from aqueous CO treatment of Wyodak coal

	with NaOH[a]	without NaOH[b]
Gaseous Product		
Hydrogen, mol %	32	8
CO, mol %	7	52
CO_2, mol %	61	34
Hydrocarbon gases, mol %	<0.5	<0.5
Water-Insoluble Prod, wt% maf	81	85
Humic acids + ether solubles, wt% maf	1.3	n.d.

a. Wyodak coal, 1000 psig CO cold, 4.2 g NaOH, 75 mL H_2O, 340 °C, 300 mL reactor.
b. Wyodak coal, 1000 psig CO cold, 40 mL H_2O, 340 °C, 300 mL reactor.

Table 2. Solubility of water-insoluble product from CO-treated coal (maf basis)

Treatment	Ultrasonic/Filtration		Soxhlet Extraction	
	THF	Pyridine (RT)	THF	Pyridine
with NaOH	78	94	55	88
without NaOH	N.A.	N.A.	54	50

Table 3. Elemental analysis of CO-treated coals

Element	Starting coal	CO-treated coal			
		with NaOH			without NaOH
		Water-Insoluble	Pyridine Soluble	Pyridine Insoluble	Water-Insoluble
Carbon	70.3	79.5	85.2	40.5	81.0
Hydrogen	4.7	5.8	6.9	2.0	5.3
Nitrogen	1.0	1.7	1.5	1.5	1.7
Sulfur	0.5	0.4	0.3	0.3	0.4
Oxygen	17.9	4.7	6.1	16.9	5.2
Ash, SO_3-free	5.5	8.0	-	38.9	6.3
H/C atomic ratio	0.80	0.88	0.97	0.59	0.79

Table 4. Elemental balance for NaOH-treated coal

	Coal	Water Insoluble Product[a]	CO_2	H_2O	Total
Carbon	70.32	66.3	4.0		70.3
Hydrogen	4.68	4.83		0.42	5.25
Nitrogen	1.04	1.42			1.42
Oxygen	17.92	3.92	10.67	3.33	17.92
Sulfur	0.5	0.33			0.33
Ash	5.54	5.54			5.54
Total	100.00	82.3	14.67	3.75	100.72

a. Ash concentration corrected to starting coal.

Table 5. Elemental Balance for 300 mL Reactor Run without NaOH

	Coal	Water-Insol Product	CO_2	H_2O	Total
Carbon	70.32	68.76	1.56		70.32
Hydrogen	4.68	4.50		1.17	5.67
Nitrogen	1.04	1.44			1.44
Oxygen	17.92	4.41	4.16	9.35	17.92
Sulfur	0.5	0.34			0.34
Ash	5.54	5.54			5.54
Total	100.00	85.00	5.72	10.52	101.23